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ON THE ACTION

OF

Ortho- and Meta-diazo-benzene-sulphonic Acids

ON

METHYL AND ETHYL ALCOHOL

With some observations on the action of nitric acid on certain alkoxy-benzene-sulphon-amides.

DISSERTATION

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BY

EDWARD CURTIS FRANKLIN.

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The work here presented was carried on in the chemical laboratory of the Johns Hopkins University at the suggestion of Professor Remsen and under his personal guidance. The author desires to record here an expression of gratitude for the instruction and advice he has received from his teacher during his residence at this University. He also acknowledges his indebtedness to Professor Williams and Professor Morse.

Baltimore, Md., May, 1894.

ON THE ACTION OF ORTHO- AND META-DIAZO-BENZENE-SULPHONIC ACIDS ON METHYL AND ETHYL ALCOHOL.

Introduction.

The investigation, an account of which is given in the following pages, was undertaken for the purpose of studying the decompositions of ortho- and meta-diazo-benzene-sulphonic acids with methyl and ethyl alcohol under different conditions of pressure and temperature.

To this work is appended some observations showing the identity of the methoxy-benzene-sulphon-amide obtained by Shober from para-diazo-benzene-sulphonic acid, with the amide of the methoxy-benzene-sulphonic acid obtained by the action of sulphuric acid on anisol, together with an account of some results of the action of fuming nitric acid on certain alkoxy-benzene-sulphon-amides.

Since the discovery of the diazo compounds by Griess in 1860, many workers have studied the manifold interesting transformations of this remarkable class of bodies. The results first reached by Griess[1] in his observations on the decompositions of diazo compounds with alcohols led him to make the general statement that when diazo compounds are decomposed by boiling alcohol the nitrogen is eliminated and hydrogen takes its place. This so-called Griess or hydrogen reaction has been found, however, not to take place in all cases, but that often an alkoxy group instead of an hydrogen atom is substituted for the diazo group.

For a number of years past systematic investigations have been in progress in this laboratory under the general direction of Professor Remsen, having for their object the determination

1. Annalen **137**, 39.

of the conditions which influence the character of the decompositions of diazo compounds with alcohols.

Researches have been conducted in turn by Palmer[1], Orndorff[2], Graham[3], Metcalf[4], Dashiell[5], Shober[6], Parks[7], Beeson[8] and Weida[9], which have brought to light many facts regarding the conditions which influence these decompositions.

It has been shown that the reactions are affected by the nature and position of the substituting groups in the diazo compound, by the complexity of the alcohol, and by the conditions of pressure and temperature under which the decompositions take place. A discussion of these relations at the present time, however, would be premature.

Preparation of Ortho- and Meta-amido-benzene-sulphonic Acids.

Meta-amido-benzene-sulphonic acid may be prepared[10] by the reduction of meta-nitro-benzene-sulphonic acid, which latter may be obtained either by the nitration of benzene-sulphonic acid or by the sulphonation of nitro-benzene.

Limpricht[11] has shown that the meta-nitro acid is not the only product of these reactions, but that at the same time quantities of the isomeric ortho and para acids are formed. The quantity of the ortho and para acids obtained by Limpricht, when benzene was first changed into the sulphonic acid and then nitrated was about 10 per cent., 90 per cent. of the product being obtained as the meta modification. When the acids were prepared by the action of fuming sulphuric acid on nitro-benzene the yield of the ortho and para acids was found to be considerably less.

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1. Am. Chem. Jour. **8**, 243.
2. Ibid. **9**, 387.
3. Ibid. **11**, 319.
4. Ibid. **15**, 301.
5. Ibid. **15**, 105.
6. Ibid. **15**, 379.
7. Ibid. **15**, 320.
8. Dissertation, 1893.
9. Dissertation, 1894.
10. Laurent Jahresber. **1850**, 418; Schmitt, Annalen **120**, 164; V. Meyer and Stuber, Annalen **165**, 164; H. Rose, Berichte **5**, 41.
11. Annalen **177**, 61.

Preparation of the nitro-sulphonic acids: 250 grams of pure benzene and 300 c. c. of fuming sulphuric acid were introduced into a flask of one liter capacity provided with a cork into which is fitted a long glass tube to serve as a reflux condenser. The reaction began at once, accompanied by considerable evolution of heat. The action was assisted by shaking, care being taken not to allow the action to proceed so rapidly as to raise the temperature of the mixture to the boiling point of benzene. At the expiration of about an hour the benzene had almost completely passed into solution. A small quantity which persistently resisted the action of the acid was removed by transferring the acid mixture to a flask of such a size that the acid mixture filled it well up into the neck. After standing a short time the benzene collected in the neck of the flask and was removed by means of a pipette. The benzene-sulphonic acid solution was then returned to the larger flask and treated with fuming nitric acid of 1.50 specific gravity. The addition of the nitric acid was made very cautiously. At the beginning of the operation the reaction was so violent that it was necessary to suspend the operation from time to time, and cool the mixture by immersion in cold water. Towards the end of the operation the action became much less violent, and finally when the addition of a considerable quantity of acid produced no further elevation of temperature the nitration was considered finished. The acid mixture was then poured into a large quantity of water and allowed to stand until a small quantity of di-nitro-benzene which had been formed, had subsided. The clear yellow liquid was then decanted and neutralized with chalk. The solution was filtered from gypsum and excess of chalk, and the calcium salts converted into the potassium salts by the addition of potassium carbonate. On filtering off the the calcium carbonate, a bright yellow solution of the potassium salts was obtained. The nitro acids might at this stage have been reduced to the amido acids and these subsequently separated, but after several attempts at

this method, it was found advisable to first separate the nitro acids from the solution and then effect their reduction in solutions free from nitric acid. If the reduction is effected in the solution containing nitrates, a black solution results, from which the amido acids can be but very imperfectly separated. The solution of the potassium salts was concentrated and set aside to crystallize. The first crops were almost pure potassium meta-nitro-benzene-sulphonate. They were reserved and reduced separately, furnishing pure meta-amido-benzene-sulphonic acid, while the latter crystallizations, which were mixtures of all three modifications, were reduced without separation from each other, furnishing a mixture of the three amido-benzene-sulphonic acids.

Reduction of Meta-nitro-benzene-sulphonic Acid: The reduction may be readily effected, either by the use of tin and hydrochloric acid, according to the method of Brackett and Hayes,[1] or by ammonium sulphide. Limpricht used the method by ammonium sulphide, which has also in this investigation been found preferable to the method by tin and hydrochloric acid.

The potassium salt was dissolved in water by the aid of heat, and the solution made strongly alkaline by the addition of ammonium hydroxide. Into the solution thus prepared hydrogen sulphide was conducted until complete saturation had taken place. The solution was then heated on a water bath until the excess ammonium sulphide was completely expelled. Hydrochloric acid was then added, the solution filtered from separated sulphur and set aside to crystallize. After standing over night the acid had separated. By re-solution of the crude acid in boiling water and treatment with bone black, a colorless solution was obtained, which when allowed to stand furnished the crystallized acid in a pure condition.

Meta-amido-benzene-sulphonic acid was thus obtained in the form of slender, colorless needles without water of crystal-

1. Am. Chem. Jour. 9, 400.

lization. It is difficultly soluble in cold water, more readily in hot. It becomes discolored by exposure, and decomposes without melting upon being heated.

Reduction of the mixture of the ortho-, meta- and para-nitro-benzene-sulphonic acids, and the separation and purification of the ortho modification: The mixture of the potassium salts of the three isomeric acids, obtained as described above, was treated with ammonium hydroxide and hydrogen sulphide as described above for the reduction of the meta acid. The acid solution, after removal of the separated sulphur, was boiled with bone black and set aside to crystallize. By proper regulation of the concentration of the solution the three acids crystallized out, each in its characteristic form. The meta modification was deposited as slender needles; the ortho in large, transparent rhombohedrons which were anhydrous, while the para acid formed thick, leaf-like crystals with water of crystallization. From the crystalline mixture thus obtained, the light, slender crystals of the meta acid were removed, by washing, from the larger and heavier crystals of the isomeric acids. The remaining mixture of the ortho and para acids was then partially dried by pressure between folds of absorbent paper, and the desiccation completed in the air bath at a temperature of 110° to 120°, by which treatment the para acid lost its water of crystallization and crumbled to powder. The anhydrous ortho acid was not affected, and was separated from the pulverulent para acid by means of a sieve. The ortho acid was then, after several re-crystallizations from hot water and treatment with bone black, obtained in a pure condition.

In one experiment, a yield of over four per cent was obtained. Other experiments were less satisfactory.

Ortho-amido-benzene-sulphonic acid was thus obtained in fine crystals of a rhombohedral habit, and usually of a pronounced pink color. It is difficultly soluble in cold water, more readily in hot water, and decomposes without melting on being heated.

The para-amido-benzene-sulphonic acid from the above mixture was purified by re-crystallization, and its identity with sulphanilic acid, prepared by the action of sulphuric acid on aniline, was confirmed. A small quantity of the acid was diazotized, the diazo compound decomposed with methyl alcohol, and the resulting methoxy-benzene-sulphonic acid converted into the amide. This amide[1] $C_6H_4 < \begin{matrix} O\text{-}CH_3 \\ SO_2NH_2 \end{matrix}$ (p) crystallized in colorless well formed needles melting at 112°.

PREPARATION OF META-DIAZO-BENZENE-SULPHONIC ACID.

Several methods of diazotizing were studied before the most satisfactory one was found. The method of Schmitt,[2] which answers satisfactorily for the para acid, and which has been found in the course of this investigation to answer especially well for the diazotation of the ortho acid, gives with the meta acid unsatisfactory results. The method consists in passing nitrous fumes (formed by the action of ordinary concentrated nitric acid on arsenious oxide) into alcohol in which is suspended the finely powdered acid. Complete diazotation could not be effected. There always remained unacted upon a considerable quantity of the amido acid. The first method described by Shober,[3] viz: solution of the acid in hot caustic soda, addition of sodium nitrite and pouring the mixture into cold dilute sulphuric acid gave a satisfactory yield, but there was always danger of contamination of the product with sodium salts or with sulphuric acid. Limpricht and Bernsden[4] prepared this diazo compound as follows: The amido acid was dissolved in hot water, and the solution brought to such a strength that, at a temperature of 50°-60°, the acid just began to separate. A rapid stream of nitrous fumes was then passed the mixture, the flask at the same time being immersed in cold water. When the action was complete the vessel was placed in ice water and left at rest for

1. Shober, Dissertation, 1892, p. 9.
2. Shober, Dissertation, 1892, p. 7.
3. Loc. cit.
4. Annalen **177**, 88.

twenty-four hours. The one objection to this method is the unsatisfactory yield due to the solubility of the diazo acid in the large quantity of water necessarily used. The following modification of the above method, which is practically the same as that described by Dashiell[1] for the preparation of para-diazo-ortho-toluene-sulphonic acid, has been found in the present case to give entirely satisfactory results: the acid in the form of moderately fine powder, was suspended in a small quantity of water (for 20 grams of the acid about 30 cc. of water) and a rapid current of nitrous fumes was conducted into the mixture until the acid had passed into solution. The mixture was kept at a temperature of 40°-50° for the reason that at this temperature the diazo compound will remain in solution instead of separating out and thus interfering with the easy recognition of the end of the reaction. When all the amido acid had passed into solution the action was considered complete. A small quantity of alcohol (10 c. c.) was added to the solution and the flask placed in a freezing mixture. The diazo compound readily crystallized out. After a few hours the diazo compound was filtered off, washed with alcohol, then with ether, and spread out on filter paper to dry. The yield was entirely satisfactory, usually equaling in weight that of the amido compound used.

Meta-diazo-benzene-sulphonic acid, as thus obtained, is a slightly colored crystalline powder. It explodes by contact with a flame or by percussion. Kept in a preparation bottle it soon shows signs of decomposition.

Apparatus for Decomposition of Diazo Compounds with Alcohols.

1. *At increased pressure.* The form of apparatus[2] used for effecting decompositions at increased pressure was the same as that described first by Palmer, and used since by a number of workers in this laboratory in studying the effect of increased

1. Dissertation, 1891.
2. Shober, Dissertation, 1892, p. 8.

pressure on the decomposition of diazo compounds with alcohols.

2. *At diminished pressure.* In carrying out the decompositions under diminished pressure, a form of apparatus in all its essentials like that described by Mr. Parks[1] was found entirely satisfactory.

3. *At atmospheric pressure.* For decompositions at atmospheric pressure, use was made of an ordinary half litre baloon flask arranged to be heated on a water bath, and provided with a reflux condenser.

Decomposition of Meta-diazo-benzene-sulphonic Acid with Methyl Alcohol.

1. *At atmospheric pressure.* Ten grams of the diazo compound together with 50 c. c. methyl alcohol were placed in the flask of the decomposition apparatus and heat applied. As the alcohol approached the boiling point, decomposition began and continued quietly to completion. About forty-five minutes were required. The product of the reaction was a strongly acid, red colored liquid. The alcohol was distilled off, the residue taken up with water and the acid neutralized with potassium carbonate. The solution was boiled with bone black, by which treatment, however, the color could not be entirely removed. The solution was then evaporated to dryness in a water bath and the desiccation completed in an air bath at 110°-120°. The complete desiccation of the residue was a tedious operation, because of the persistence with which the dark brown, viscous mass retained water. After once dry, however, it showed no marked tendency to absorb moisture from the atmosphere. Nine grams of the crude potassium salt were obtained as a strongly colored, difficultly pulverizable mass. The powdered salt was mixed with an equal weight of phosphorus pentachloride. As soon as the two substances were well mixed vigorous action took place which was assisted and carried to completion by heating

1. Dissertation. 1893.

the the mixture for a time on the water bath. On cooling, the mass was treated with water, and the crude liquid chlorides thus obtained, after thorough washing with water, were covered with a large excess of concentrated ammonia solution and left over night. The excess of ammonia was then removed by evaporation on a water bath; the residue, after cooling, was pulverized and washed with a small quantity of cold water to remove ammonium chloride. The crude amides which were mixed with a considerable quantity of "gummy" impurities, were then taken up with hot water, the solution boiled with bone black and set aside to crystallize. The crystals were contaminated by the sticky material above mentioned, from which they were separated by repeated re-crystallization. 2.5 grams of pure amide melting at 130° were obtained.

From the mother liquors a crop of mixed crystals was obtained, from which could be picked out mechanically, slender needles melting at 128°-130°, and thicker, stouter ones melting at about 147°. A small quantity of the latter were separated and re-crystallized. The resulting crystals melted at 151° and were hence without doubt benzene-sulphonamide. [Benzene-sulphon-amide melts at 151°-156°].

In this experiment both the methoxy and the hydrogen reactions took place, the methoxy reaction greatly predominating.

2. *At atmospheric pressure plus 850 mm. of mercury.* Ten grams of the diazo compound together with 100 c. c. methyl alcohol were introduced into the pressure flask and decomposition carried out at the above indicated pressure. The flask was heated rapidly in order that the full pressure might be reached with little loss of time, the object of which procedure was to bring about as much of the decomposition as possible at the chosen pressure. After the full pressure was reached the decomposition proceeded rapidly to the end which was reached in about five minutes from the time of application of the flame. The product of the reaction was scarcely to be

distinguished in appearance from the corresponding product in the last experiment. The alcohol was removed by distillation and the residue converted into the amide as described in the previous experiment. The yield of pure methoxy-benzene-sulphon-amide was about the same as in the previous experiment. From the mother liquors additional crops of the methoxy product were obtained, but no benzene-sulphon-amide could be found.

3. *At atmospheric pressure minus 450 mm. of mercury.* Four grams of the diazo compound and 50 c. c. methyl alcohol were placed in the flask of the apparatus for decomposition under diminished pressure, and after regulating the pressure, the contents were heated to boiling. The reaction proceeded very slowly and was complete only after six to seven hours. The resulting product, presenting the same appearance as those obtained under the conditions of the above described experiments, was treated for the amides. These amides were also so much contaminated with the gummy material that their isolation and purification was accompanied by considerable loss. 0.36 gram of the pure methoxy-benzene-sulphon-amide was obtained. From the concentrated mother liquors crystals were separated which melted at 145°-150°. The hydrogen reaction therefore accompanies the methoxy reaction under the conditions of this experiment.

Meta-methoxy-benzene-sulphon-amide crystallizes in colorless needles. It is sparingly soluble in cold water, more readily in hot water and in alcohol.

That this amide is the meta-methoxy-benzene-sulphon-amide is shown by sulphur determinations and by its melting point, 130° [Lagai[1] found it to melt at 130°].

Determinations of sulphur gave the following results:

I. 0.2265 gram of the substance gave 0.2822 gram barium sulphate which corresponds to 17.13 per cent. sulphur.

II. 0.2138 gram of the substance gave 0.2656 gram barium sulphate which corresponds to 17.08 per cent. sulphur.

1. Berichte **1892**, 1839.

The calculated percentage of sulphur in $C_6H_4(OCH_3)(SO_2NH_2)$ is 17.11.

The synthesis of meta-methoxy-benzene-sulphon-amide from benzene is indicated as follows:

(1) $C_6H_6+H_2SO_4=C_6H_5SO_2OH+H_2O.$

(2) $C_6H_5SO_2OH+HNO_3=C_6H_4<\begin{matrix}NO_2\\SO_2OH\end{matrix}+H_2O.$

(3) $C_6H_4<\begin{matrix}NO_2\\SO_2OH\end{matrix}+6H=C_6H_4<\begin{matrix}NH_2\\SO_2\end{matrix}>O+2H_2O.$

(4) $2C_6H_4<\begin{matrix}NH_2\\SO_2\end{matrix}>O+N_2O_3=2C_6H_4<\begin{matrix}N_2\\SO_2\end{matrix}>O+3H_2O.$

(5) $C_6H_4<\begin{matrix}N_2\\SO_2\end{matrix}>O+CH_3OH=C_6H_4<\begin{matrix}O\text{-}CH_3\\SO_2OH\end{matrix}-N_2$

(6) $C_6H_4<\begin{matrix}O\text{-}CH_3\\SO_2OK\end{matrix}+PCl_5=C_6H_4<\begin{matrix}O\text{-}CH_3\\SO_2Cl\end{matrix}+POCl_3+KCl.$

(7) $C_6H_4<\begin{matrix}O\text{-}CH_3\\SO_2Cl\end{matrix}+NH_3=C_6H_4<\begin{matrix}O\text{-}CH_3\\SO_2NH_2\end{matrix}+HCl.$

Decomposition of Meta-diazo-benzene-sulphonic Acid with Ethyl Alcohol.

1. *At atmospheric pressure.* Ten grams of the diazo compound and 50 c. c. ethyl alcohol were heated together in the decomposition apparatus, with the result that the diazo compound was decomposed and in solution at the expiration of twenty minutes. The solution of the acids thus formed presented the same general appearance as those obtained when methyl alcohol was used. The residue, however; was darker, somewhat more difficult to dry, and furnished amides which were more contaminated with the "gummy" impurities than the amides obtained when the methyl alcohol was used. Upon treating the reaction product for the amides as described for the methyl alcohol products, a crop of crystals was obtained in which the two amides could be readily distinguished. The better formed, more slender needles could easily be removed in sufficient quantity for melting point determinations. They were found to melt at 131°,

showing them to be meta-ethoxy-benzene-sulphon-amide. [Lagai[1] found meta-ethoxy-benzene-sulphon-amide to melt at 131°]. The crystals of the shorter, stouter habit were found to melt at 150°, and were consequently benzene-sulphon-amide. As nearly as could be estimated the two amides were formed in about equal quantities.

In a second experiment carried out under the same condition, similar results were reached. From 3 grams of the diazo compound 0.3 gram of the mixed amides in a pure condition were obtained.

2. *At atmospheric pressure plus 850 mm. of mercury.* Ten grams of the diazo compound and 100 cc. ethyl alcohol were placed in the pressure flask and decomposed at the above indicated pressure. The decomposition took place readily and was complete in about ten minutes. From the product, treated in the usual way for the amides, 1.5 gram pure ethoxy-benzene-sulphon-amide melting at 131° were obtained. The mother liquors gave additional crops of the ethoxy-amide, and it was only in the residual concentrated mother liquor that a crop of crystals was obtained in which the presence of benzene-sulphon-amide crystals was recognized by their habit, and by a determination of the melting point of the substance.

A second experiment, carried out as above described, gave somewhat over a gram of the pure ethoxy-benzene-sulphon-amide, while the proportional quantity of the benzene-sulphon-amide present was estimated to be somwhat greater.

Meta-ethoxy-benzene-sulphon-amide crystallizes in colorless needles very similar in appearance to meta-methoxy-sulphon-amide. It is scarcely soluble in cold water, and less soluble in hot water than its simpler homologue.

A determination of sulphur gave the following results: 0.1134 gram of the substance gave 0.1336 gram barium sulphate, which corresponds to 16.19 per cent. sulphur. The calculated percentage of sulphur in $C_6H_4(OC_2H_5)(SO_2NH_2)$ is 15.92.

1. Ber. **23**, 3392.

Preparation of Ortho-diazo-benzene-sulphonic Acid.

After coming into possession of a quantity of the ortho-amido-benzene-sulphonic acid, an excellent yield of the diazo compound could be obtained by suspending the acid in ordinary alcohol and passing a stream of nitrous fumes into the mixture, the method being the same as that described by Metcalf[1] and by Shober[2] for thepreparation of para-diazo-meta-toluene-sulphonic acid and para-diazo-benzene-sulphonic acid respectively. The diazotation of the ortho-amido-benzene-sulphonic acid takes place with remarkable ease.

Ten grams of the finely powdered amido acid were suspended in 25 cc. ordinary alcohol and a rapid stream of nitrous fumes passed into the mixture. The contents of the flask became warm but the temperature was not allowed to rise above 40°-50°. In about ten minutes the diazotation was complete. An equal volume of ether was then added to the mixture, and the flask with its contents left at rest in a freezing mixture of ice and salt for several hours. The diazo compound was then filtered off, washed with ether and spread out on filter paper to dry. A yield of 10 grams was obtained. Ortho-diazo-benzene-sulphonic acid thus prepared is a beautifully white crystalline powder, which slowly becomes colored on exposure. It is comparatively stable and if protected from air and moisture it may be kept for a considerable time without suffering appreciable change. It explodes by contact with flame or by percussion.

The Relative Susceptibility of the Ortho-, Meta- and Para-amido-benzene-sulphonic Acids to the Action of Nitrous Acid.

It is interesting to compare, in passing, the relative susceptibilities of the three isomeric amido-benzene-sulphonic acids to the action of nitrous acid. Meta-amido-benzene-sulphonic acid cannot be satisfactorily diazotized by treatment

1. Dissertation, 1890, p. 4.
2. Dissertation, 1892, p. 7.

in suspension in alcohol with nitrous fumes, as the author has determined by repeated trials. Suspended in water, however, it is diazotized without the least difficulty.[1] The para-amido-benzene-sulphonic acid must, according to Shober,[2] be very finely powdered. When this preliminary has been properly attended to, a quantity of the acid suspended in alcohol can be diazotized in from one to two hours time. It has been determined in the present investigation that the para acid is diazotized with much more difficulty under the above conditions than is the ortho acid. Mr. Daniel Base, working in this laboratory, found it quite impossible to effect complete diazotation of sulphanilic acid by this method. There always remained behind, when the diazo acid was decomposed, a residue of sulphanilic acid. The remarkable ease with which the ortho acid can be diazotized under these conditions is evident from the description of its preparation above. Similar relations between the para-toluidine-ortho-sulphonic acid and the para-toluidine-meta-sulphonic acid have been pointed out by Metcalf.[3] The latter compound, in which the amido and sulphonic acid groups occupy the ortho position relatively to each other, is readily diazotized by suspension in alcohol, while the former acid, in which these two groups occupy the meta position relatively to each other, cannot satisfactorily be so diazotized. It is of course recognized that differences of solubility of the amido compound may account for their observed behavior when suspended in alcohol.

Decomposition of Ortho-diazo-benzene-sulphonic Acid with Methyl Alcohol.

1. *At atmospheric pressure.* Three grams of the diazo compound and 25 c. c. methyl alcohol were heated in a flask with reflux condenser. The reaction was complete in twenty minutes, yielding a clear and but slightly colored solution.

1. See page 11.
2. Dissertation, 1892, p. 7.
3. Dissertation, 1892, p. 4.

The decomposition products were treated in the usual manner for the amides. 0.8 gram of pure methoxy-benzene-sulphon-amide, melting at 171°, was obtained, while no benzene-sulphon-amide could be found. The amides in every case of decomposition of the ortho acid were found to be less contaminated with the gummy impurities than were the decomposition products of the meta acid.

2. *At atmospheric pressure plus 850 mm. of mercury.* Three grams of the diazo compound, together with 100 c. c. methyl alcohol, were introduced into the pressure flask and the decomposition carried out at the above indicated pressure. The reaction was complete in five minutes, furnishing a clear and but slightly colored solution. The alcohol was removed by distillation, and the residue treated as usual for the amides. Only the methoxy-benzene-sulphon-amide, melting at 171°, could be identified.

3. *At atmospheric pressure minus 450 mm. of mercury.* Five grams of the diazo compound, together with 60 c. c. methyl alcohol, were introduced into the flask of the apparatus for decomposition at diminished pressure, and after adjustment of the pressure, the contents of the flask were heated to boiling. The solution slowly took on a light red color, and after about seven hours boiling the decomposition was complete. The alcohol was removed by distillation, and the residue treated as in the foregoing experiments for the amides. 1.54 grams of methoxy-benzene-sulphon-amide, melting at 171°, were obtained, while from the mother liquors no benzene-sulphon-amide could be separated.

Ortho-methoxy-benzene-sulphon-amide crystallizes in colorless needles which are but sparingly soluble in cold water, more readily soluble in hot water or in alcohol.

A determination of sulphur in the amide obtained in these experiments resulted as follows: 0.2242 gram of the substance gave 0.2777 gram barium sulphate, which corresponds to 17.04 per cent. sulphur. The percentage of sulphur calculated for $C_6H_4(O\text{-}CH_3)(SO_2NH_2)$ is 17.11.

Further proof of the identity of this compound was furnished by chlorine and sulphur determinations in the ortho-methoxy-benzene-sulphon-chloride, which compound has also been prepared by Haitinger.[1]

Preparation of Ortho-methoxy-benzene-sulphon-chloride.

Fifteen grams of ortho-diazo-benzene-sulphonic acid were decomposed with 125 c. c. methyl alcohol at a pressure of 850 mm. above atmospheric pressure. The reaction was complete in forty-five minutes, furnishing as a product a clear and but slightly colored solution. The acid liquid was neutralized with pure barium carbonate and the attempt made to obtain a pure barium salt. A quantity of crystals were obtained which were in all probability the impure barium salt, but which were not further studied, as it seemed more desirable to use the material for the preparation of the chloride. The barium salt was changed into the potassium salt, and this, by the usual method with phosphorus pentachloride, was converted into the acid chloride. As noticed when working with smaller quantities in the experiments above, this chloride separated from the reaction mixture, on treatment with water, as a waxy solid. It was washed with water and dissolved in ether. The ethereal solution was dried with calcium chloride, filtered, and placed in a desiccator to crystallize. From the concentrated solution the chloride separated in nearly colorless plates, which upon re-crystallization from petroleum ether (B. P., below 100°) was deposited as stout needles. It was found to melt at 56°. Haitinger[2] prepared this chloride from ortho-phenol-sulphonic acid and found its melting point to be 55°.

Determinations of chlorine and sulphur in this compound gave the following results:

I. 0.2266 gram of the substance gave 0.1585 gram silver chloride, which corresponds to 17.29 per cent. chlorine. The

1. Monatshefte, 4, 173.
2. Loc. cit.

percentage of chlorine calculated for $C_6H_4(O\text{-}CH_3)(SO_2Cl)$ is 17.19.

II. 0.2030 gram of the substance gave 0.2335 gram barium sulphate, which corresponds to 15.81 per cent. sulphur. The percentage of sulphur calculated for $C_6H_4(O\text{-}CH_3)(SO_2Cl)$ is 15.50.

Decomposition of Ortho-diazo-benzene-sulphonic Acid with Ethyl Alcohol.

1. *At atmospheric pressure.* Five grams of the diazo compound and 75 c. c. ethyl alcohol were placed in the flask of the decomposition apparatus, and the reaction carried out as usual. In from five to seven minutes the decomposition was completed. The resulting light red colored solution was treated in the usual manner for the amides. The only amide obtained was an ethoxy-benzene-sulphon-amide, melting at 156°.

2. *At atmospheric pressure plus 850 mm. of mercury.* Five grams of the diazo compound, together with 75 c. c. ethyl alcohol were introduced into the pressure flask and the decomposition initiated under full pressure, but because of an accident it was completed at atmospheric pressure. 0.75 gram of the pure ethoxy-benzene-sulphon-amide, melting at 156°, was obtained.

Whether or not the hydrogen reaction takes place in these decompositions could not be definitely determined from the above experiments. The melting points of the two compounds, ortho-ethoxy-benzene-sulphon-amide and benzene-sulphon-amide, lie so near together that determinations of these constants could not be made use of as guides. Repeated attempts to obtain crops of mixed crystals of different habit, from the mother liquors were unsuccessful. This, together with the fact that the amide obtained showed a constant melting point, led to the conclusion that the hydrogen reaction did not take place.

A sulphur determination resulted as follows: 0.2203 gram of the subtance gave 0.2547 gram barium sulphate, which corresponds to 15.89 per cent. sulphur. The calculated percentage of sulphur in $C_6H_4(O\text{-}C_2H_5)(SO_2NH_2)$ is 15.92.

Ortho-ethoxy-benzene-sulphon-amide crystallizes from hot dilute alcohol as colorless, slender needles. It is almost completely insoluble in cold water and but sparingly soluble in hot water.

G. T. Moody[1] prepared the ortho-ethoxy-benzene-sulphon-amide by the ethylation of para-brom-phenol, sulphonation of the brom-phenetol thus formed, reduction of the brom-phenetol-ortho-sulphonic acid, and conversion of the resulting acid into its amide. He found its melting point to be 156°.

Comparison of the Methoxy-benzene-sulphon-amide obtained from Sulphanilic Acid with that prepared from Anisol.

With the object in view of making the comparison, Mr. Shober[2] submitted anisol to the action of ordinary concentrated sulphuric acid, and obtained, instead of a mono-sulphonic acid, an anisol-di-sulphonic acid. This result was surprising, as Zervas[3], in order to make the di-sulphonic acid, had made use of fuming sulphuric acid. Kekulé[4] states that by the action of sulphuric acid on anisol, both the para- and the ortho-anisol-mono-sulphonic acids are formed. Contrary, however, to the statements of Kekulé and the results of Lagai,[5] G. T. Moody,[6] in his studies on the sulphonic acids derived from the anisoïls, finds that only the para modification can be obtained. In the present investigation, in conformity with the results of Moody, but one amide has been isolated from the product of the action of sulphuric acid on anisol.

1. Proc. Chem. Soc., 1892-3, p. 214.
2. Dissertation, 1892, p. 20.
3. Annalen **103**, 342.
4. Ztschr. f. Chem. **1867**, 201.
5. Berichte **25**, 1839.
6. Proc. Chem. Soc., 1892-3, p. 90.

For the purpose of making the desired comparisons, quantities of the methoxy-benzene-sulphon-amides were prepared by each of the following processes:

1. *Methoxy-benzene-sulphon-amide from sulphanilic acid.* The method followed was that described by Shober.[1] Sulphanilic was diazotized by suspending the finely powdered acid in ordinary alcohol and passing into the mixture a current of nitrous fumes. A satisfactory yield of the diazo-compound, not entirely free however from sulphanilic acid, was obtained. The well-dried diazo-compound was decomposed with methyl alcohol at 850 mm. above atmospheric pressure in order to increase as much as possible the yield of the methoxy-compound. The product of the reaction was treated in the usual way for the amides. From 45 grams of the crude sodium salts about 8 grams of the pure methoxy-benzene-sulphon-amide, melting at 112°, were obtained. The mother liquors furnished crops of mixed crystals in which the presence of benzene-sulphon-amide was recognized both by its habit and by melting point determinations. The results obtained by Shober, namely, that the alkoxy-reaction predominates under the above conditions were confirmed.

2. *Methoxy-benzene-sulphon-amide from anisol.* Thirty grams anisol (made by Mr. J. L. Beeson,[2] dried and redistilled—B. P. 152°-154°) was poured into three times its weight of ordinary concentrated sulphuric acid. The ether dissolved with slight elevation of temperature. After heating, in one case for two hours on the water bath, in another for one hour at 80°, the acid mixture was poured into a large quantity of water and neutralized with barium carbonate. A portion of the barium salt was crystallized out in the form of slightly yellowish, tubular crystals, which were not further studied. The remaining portion of the barium salt was converted into the sodium salt, a quantity of which, in the form of short, slender needles, containing water of crystallization, was also

1. Dissertation, 1892, p. 7.
2. Dissertation, 1893, p. 22.

reserved. The solution of the sodium salt was evaporated to dryness and the desiccation completed in an air bath at 110°. The dry salt was finely powdered and intimately mixed with an equal weight of phosphorus pentachloride. Action took place at once. After heating for a time on the water bath, the dish was set aside to cool. The mass was then treated with water and the oily chloride which separated was well washed with water and converted into the amide by the action of concentrated ammonia solution. The excess of ammonia was removed by evaporation on a water bath, the residue after cooling, washed with a small quantity of cold water to remove ammonium chloride, and the crude amide purified by repeated re-crystallization from hot water and treatment with bone-black. A satisfactory yield of methoxy-benzene-sulphon-amide, melting at 112°, was obtained.

A determination of sulphur in the compound gave the following results: 0.1785 gram of the substance gave 0.2243 gram barium sulphate, which corresponds to 17.19 per cent. sulphur. The calculated percentage of sulphur in $C_6H_4(O\text{-}CH_3)(SO_2NH_2)$ is 17.11.

From another portion of the sodium salt the acid chloride was made, which when crystallized from ether was obtained in the form of colorless, six-sided plates, melting at 40°. Moody[1] found this chloride to melt at 40.5°.

The amides obtained in these two described experiments present exactly the same appearance. They crystallize in long, slender, colorless needles, are difficultly soluble in cold water, more readily so in hot, and melt at 112°.

These two products were further compared by a study of their behavior toward fuming nitric acid.

Shober[2] found one of the products of the action of fuming nitric acid on the methoxy-amide obtained from sulphanilic acid to be meta-di-nitro-benzene, as was shown by a determination of its melting point (88°), by the absence

1. Loc. cit.
2. Dissertation, 1892, p. 22.

of sulphur from its composition, and by the fact that by reduction with tin and hydrochloric acid and subsequent treatment with sodium nitrite the yellow color characteristic of phenylene-di-amine was obtained.

COMPARISON OF THE BEHAVIOR OF THE METHOXY-BENZENE-SULPHON-AMIDES OBTAINED RESPECTIVELY FROM SULPHANILIC ACID AND ANISOL TOWARDS FUMING NITRIC ACID.

The amide from sulphanilic acid. Four grams of the amide were added gradually to 15 grams of ordinary fuming nitric acid. The action was very vigorous. The acid was kept cool by immersion of the containing vessel in cold water. The addition of amide was made slowly and in small quantities. Upon dilution of the acid solution a yellow substance separated out, which when purified by re-crystallization from alcohol was found to melt at 88°. About 0.5 gram of the substance, meta-di-nitro-benzene, was obtained.

The amide from anisol. Four grams of the methoxy-benzene-sulphon-amide, prepared from anisol, were treated in the manner described in the last experiment, with entirely similar results, excepting that a larger quantity, nearly a gram, of di-nitro-benzene was obtained. A test for sulphur in this product, by the method of Carius, gave a negative result. A small quantity of the nitro-compound, by reduction with ammonium sulphide furnished meta-nitraniline, which crystallized in the characteristic slender, yellow needles, and melted at 114°.

Meta-di-nitro-benzene is hence one of the products of the action of nitric acid on para-methoxy-benzene-sulphon-amide, which latter substance further, is obtained either by the decomposition of para-diazo-benzene-sulphonic acid with methyl alcohol, or by the action of sulphuric acid on anisol, and subsequent conversion of the acid thus formed into the amide.

The small yield of the di-nitro-benzene obtained by the action of nitric acid on para-methoxy-benzene-sulphon-amide

suggests the question as to what other substances may be formed.

ACTION OF FUMING NITRIC ACID ON ALKOXY-BENZENE-SULPHON-AMIDES.

1. *On Para-methoxy-benzene-sulphon-amide:* That meta-di-nitro-benzene is not the only product of the action of nitric acid on this amide was suspected because of the small yield of the nitro product obtained above. In order to determine what other compounds might be formed, 4.4 grams para-methoxy-benzene-sulphon-amide were added gradually to 10 grams of fuming nitric acid, of specific gravity 1.52, kept cold by a freezing mixture of ice and salt. It was observed that when the temperature of the acid was kept well down the quantity of meta-di-nitro-benzene formed was always much lessened. The acid liquid was diluted with water, which caused a separation of a small quantity of di-nitro-benzene. This was filtered off, and the filtrate evaporated with alcohol for the purpose of removing the excess of acid. The thick syrupy residue was diluted with water and neutralized with potassium hydroxide when immediately a crop of crystals of the potassium salt of an acid of the composition given below was obtained.

The analysis of the compound yielded the following results:

I. 0.3498 gram gave 0.4021 gram carbon di-oxide and 0.0751 gram water.

II. 0.2854 gram gave 13.9 c. c. nitrogen, measured over water at a temperature of 18°, and 726 mm. barometric pressure.

III. 0.1265 gram gave 0.1127 gram barium sulphate.

IV. 0.1448 gram gave 0.0467 potassium sulphate.

	Calculated for $C_7H_6O_6NSK$	Found I.	II.	III.	IV.
C	31.00	31.34			
H	2.21	2.38			
N	5.17		5.31		
S[1]	11.81			12.23	
K	14.38				14.46

1. The fuming nitric acid used was found to contain sulphuric acid.

The principal product of the action of nitric acid on para-methoxy-benzene-sulphon-amide is hence a mono-nitro-para-methoxy-benzene-sulphonic acid of the formula:

$$C_6H_3\begin{cases}NO_2 & (?)\\ O\text{-}CH_3 & (1)\\ SO_2OH & (4)\end{cases}$$

A portion of this acid was reduced to the amido-compound, while another was converted into the sulphon-amide by successive treatment with phosphorus pentachloride and ammonium hydroxide. The sulphon-amide was obtained as well formed, yellow needles melting at 138°-140°. These products will be analyzed.

2. *On meta-methoxy-benzene-sulphon-amide.* Three grams of the amide were added gradually to 10 grams of fuming nitric acid. The experiment was carried out as nearly as possible in the same manner as described for the corresponding para compound. No di-nitro-benzene was obtained.

A second experiment, in which 5 grams of the amide and 20 grams of the acid were used, also failed to give any di-nitro-benzene. The solutions from these two experiments were united, and evaporated with alcohol to remove the excess of nitric acid. The residue was taken up with water and neutralized with barium carbonate. The filtered solution, after boiling with bone black and concentration, deposited crystals of a barium salt of a nitro-sulphonic acid. This salt deflagrated when heated on platinum foil, and a test for sulphur showed it to contain this element. It has not yet been analyzed.

3. *On ortho-methoxy-benzene-sulphon-amide.* One gram of the amide was added to 4 grams of fuming nitric acid as in the previous experiments. Upon dilution a small quantity of yellow needles of meta-di-nitro-benzene, melting at 88°, crystallized out.

4. *On para-ethoxy-benzene-sulphon-amide.* Two and one-half grams of the amide, added as in the above experiments to 10 grams of fuming nitric acid, gave on dilution a consider-

able yield of di-nitro-benzene. This substance, after being once re-crystallized from dilute alcohol, melted at 83°-84°.

TABLE SHOWING THE RESULTS OF THE DECOMPOSITIONS OF THE DIAZO-BENZENE-SULPHONIC ACIDS WITH

1. *Methyl alcohol:*

	At Atmospheric Pressure minus 450 mm. Mercury.	*At Atmospheric Pressure.*	*At Atmospheric Pressure plus 850 mm. Mercury.*
Ortho Acid.....	METHOXY	METHOXY	METHOXY
Meta Acid.....	METHOXY Hydrogen	METHOXY Hydrogen	METHOXY
Para Acid[1]..	HYDROGEN	HYDROGEN Methoxy	METHOXY Hydrogen

2. *Ethyl alcohol:*

		At Atmospheric Pressure.	*At Atmospheric Pressure plus 850 mm. Mercury.*
Ortho Acid.....		ETHOXY	ETHOXY
Meta Acid.....		ETHOXY HYDROGEN	ETHOXY Hydrogen
Para Acid[1].....		HYDROGEN	HYDROGEN

CONCLUSION.

The more important results reached in this investigation may be summarized as follows:

1. When meta-diazo-benzene-sulphonic-acid is decomposed with methyl alcohol under various conditions of pressure, both the alkoxy and the hydrogen reactions take place; the alkoxy reaction always predominating. These two reactions are represented by the following equations:

$$C_6H_4<\begin{matrix}N_2\\SO_2\end{matrix}>O\ {}^{(1)}_{(3)} + CH_3OH = C_6H_4<\begin{matrix}O\text{-}CH_3\\SO_2OH\end{matrix}\ {}^{(1)}_{(3)} + N_2.$$

$$C_6H_4<\begin{matrix}N_2\\SO_2\end{matrix}>O\ {}^{(1)}_{(3)} + CH_3OH = C_6H_5\,SO_2OH + CH_2O + N_2.$$

1. Shober, Dissertation, 1892.

2. When meta-diazo-benzene-sulphonic acid is decomposed with ethyl alcohol both reactions take place; at increased pressure the alkoxy reaction predominates. These reactions are represented by the following equations:

$$C_6H_4<^{N_2}_{SO_2}>O\,^{(1)}_{(3)} + C_2H_5OH = C_6H_4<^{O\text{-}C_2H_5\ (1)}_{SO_2OH\ (3)} + N_2.$$

$$C_6H_4<^{N_2}_{SO_2}>O\,^{(1)}_{(3)} + C_2H_5OH = C_6H_5SO_2OH + C_2H_4O + N_2.$$

3. When ortho-diazo-benzene-sulphonic acid is decomposed with methyl alcohol the methoxy product only is obtained, as represented by the equation:

$$C_6H_4<^{N_2}_{SO_2}>O\,^{(1)}_{(2)} + CH_3OH = C_6H_4<^{O\text{-}CH_3\ (1)}_{SO_2OH\ (2)} + N_2.$$

4. When the decomposition of ortho-diazo-benzene-sulphonic acid is effected with ethyl alcohol the alkoxy reaction only takes place, as represented by the equation:

$$C_6H_4<^{N_2}_{SO_2}>O\,^{(1)}_{(2)} C_2H_5OH = C_6H_4<^{O\text{-}C_2H_5\ (1)}_{SO_2OH\ (2)} + N_2.$$

5. Higher pressures favor the alkoxy reaction.

6. The yield of the alkoxy-amide is greater when the decomposition of the diazo compound is made with the simpler alcohol.

7. The methoxy-benzene-sulphonic acid prepared from sulphanilic acid is identical with the methoxy-benzene-sulphonic acid obtained by the action of sulphuric acid on anisol. The following equations represent the preparation of para methoxy-benzene-sulphon-amide:

a. From sulphanilic acid:

$$2C_6H_4<^{NH_2}_{SO_2}>O\,^{(1)}_{(4)} + N_2O_3 = 2C_6H_4<^{N_2}_{SO_2}>O\,^{(1)}_{(4)} + 3H_2O.$$

$$C_6H_4<^{N_2}_{SO_2}>O\,^{(1)}_{(4)} + CH_3OH = C_6H_4<^{O\text{-}CH_3\ (1)}_{SO_2OH\ (4)} + N_2.$$

b. From anisol:

$$C_6H_5\text{-}O\text{-}CH_3 + H_2SO_4 = C_6H_4<^{O\text{-}CH_3\ (1)}_{SO_2OH\ (4)} + H_2O.$$

8. When para-methoxy- or para-ethoxy-benzene-sulphon-amide is treated with fuming nitric acid one of the products is meta-di-nitro-benzene. At the same time a nitro substitution product of para-methoxy-benzene-sulphonic acid is formed as represented by the equation:

$$C_6H_4\begin{matrix}O\text{-}CH_3\\SO_2NH_2\end{matrix} + 2HNO_3 = C_6H_3\begin{matrix}NO_2\ (?)\\O\text{-}CH_3\ (1)\\SO_2OH\ (4)\end{matrix} + NH_4NO_3.$$

9. When meta-methoxy-benzene-sulphon-amide is treated with fuming nitric acid, no meta-di-nitro-benzene is formed.

10. When ortho-methoxy-benzene-sulphon-amide is treated with fuming nitric acid one of the products formed is meta-di-nitro-benzene.

NOTE.

The temperatures given in this dissertation are all uncorrected.

The alcohols used were dried over quick-lime.

The methyl alcohol was "free from acetone."

"Nitrous fumes" were made by the action of ordinary concentrated nitric acid on arsenic tri-oxide.

Biographical.

The author of this dissertation was born at Geary City, Doniphan County, Kansas, on the first day of March, 1862. His early training was received in the public schools at Doniphan, Kansas. In 1884 he entered the University of Kansas, from which institution he was graduated in 1888. He has since held the position of assistant in chemistry in the University of Kansas, with the exception of two and one-half years, of which time one-half year was spent as chemist on a sugar plantation in Louisiana, one year, 1890-1, as student in the University of Berlin, and the present year which has been given to the study of chemistry and mineralogy in the Johns Hopkins University.